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(54) Catalysts for hydrotreating hydrocarbons and method of activating the same.

(57) New supported catalysts for hydrotreating hydrocarbons comprise (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) selected from the group consisting of mercapto-carboxylic acids (including alkali metal, alkaline earth metal and ammonium salts thereof, and esters thereof), bivalent mercaptans, amino-substituted mercaptans, and thiocarboxylic acids. These new catalysts can be easily activated by treatment in the presence of hydrogen gas at a temperature in the range from room temperature to 400°C, showing higher activity than those activated by conventional methods.

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CATALYSTS FOR HYDROTREATING HYDROCARBONS AND METHOD OF ACTIVATING THE SAME

BACKGROUND OF THE INVENTION

5 (Field of the Invention)

This invention relates to catalysts for hydrotreating hydrocarbon oil that can be easily activated, and to a method of activating the same.

10

(Description of the Prior Art)

15 For the so-called hydrotreating process (treatment of hydrocarbon oil in the presence of hydrogen to effect hydrogenation, hydrodesulfurization, hydrodenitrification and hydrogenolysis), have been used those catalysts which comprise, as active ingredient, at least one member selected from the group consisting of the metals in the Periodic Table's Groups VI and VIII and are supported on an inorganic oxide carrier, such as alumina, silica-alumina and titania. Molybdenum and tungsten are frequently used as the Group VI metal, 20 and cobalt and nickel are often employed as the Group VIII metal.

These metals, usually supported on a carrier in the form of inactive oxide, must be activated before use by presulfiding for conversion from the oxide to sulfide form.

This presulfiding is generally effected by charging the catalyst to be activated in a reactor for hydrotreatment of hydrocarbon oil and passing a sulfurizing agent together with hydrogen gas through the catalyst bed. The conditions of this presulfiding vary with the type of intended hydrotreatment process and 25 the kind of sulfurizing agent used. When hydrogen sulfide is employed as the sulfurizing agent, it is diluted with hydrogen gas to a concentration of about 0.5 to 5 volume % and the resulting gaseous mixture is passed at a temperature higher than 180°C (usually higher than 250°C) in an amount of 1000 to 3000 liters (at standard temperature and pressure) for 1 liter of catalyst. When carbon disulfide, n-butylmercaptan, 30 dimethyl sulfide or dimethyl disulfide is used, it is diluted before use with light hydrocarbon oil and sulfurization is carried out at a temperature of 250 to 350°C, under a pressure of 20 to 100 Kg/cm², at a liquid space velocity of 0.5 to 2 hr⁻¹ and with a hydrogen/oil ratio of 200 to 1000 Nl/l. After finishing this presulfiding of catalyst, feedstock to be treated is fed to the reactor to start the hydrotreatment process.

This presulfiding step, on which successful operation of the succeeding hydrotreatment process 35 depends, must be performed with great care by using proper materials. When a diluent is used, for example, a hydro carbon oil containing no olefin must be selected, as otherwise the catalyst is poisoned by the polymeric substances formed from the olefins contained. In addition, heavy oil is unsuitable as the diluent because of its poor wetting on catalyst surface due to the high viscosity. As a result, light hydrocarbon oil has to be used as the diluent, leading to an increase in production cost. Furthermore, the 40 sulfurizing agent must be used in a relatively large amount to prevent the catalyst reduction from being inactivated by the reaction with hydrogen at high temperatures, and hence the weight ratio of sulfurizing agent to hydrogen must be maintained at a proper level throughout the presulfiding process. This preliminary step is rarely automated, and requires unusual and cumbersome operations, imposing a heavy burden on the operators. Thus, how to eliminate this presulfiding step, or how to minimize the cumbersome 45 operations involved, has been a subject of major concern.

A method to meet this demand was recently proposed, which comprises impregnating a supported catalyst of an active metal with a polysulfide represented by the general formula of R-S_n-R' (wherein n is an integer of 3 to 20, and R and R' are each hydrogen atom or an organic group of 1 to 150 carbon atoms), and heat-treating the polysulfide-impregnated catalyst in the absence of hydrogen gas at a temperature of 50 65 to 275°C and under a pressure of 0.5 to 70 bar [Japanese Patent Kokai No.111144 (1986)]. This method, in which the active metal is sulfurized by the polysulfide contained in the catalyst upon heating, eliminates the use of any sulfurizing agent and a diluent thereafter when presulfiding is allowed to proceed inside the reactor, thus simplifying the operation. This method also makes it possible to effect presulfiding

outside the reactor and to start hydrotreatment process immediately after the sulfurized catalyst is charged in the reactor. However, the polysulfide has to be used in the form of a solution in an organic solvent for impregnation, and hence a special contrivance is needed for the use of organic solvents in carrying out the impregnation process.

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SUMMARY OF THE INVENTION

10 The object of this invention is to eliminate the aforementioned problems associated with the conventional catalysts, and to provide a new catalyst for hydrotreating hydrocarbon oil that can be easily sulfurized for activation and a method of activating the same.

Comprehensive studies to seek for new sulfurizing agents easier to handle than the above-mentioned polysulfides have led us to find that organic compounds having mercapto radical (-SH) are best suited for 15 the purpose. This invention was accomplished based on these findings.

Thus, the first aspect of this invention relates to a catalyst for hydrotreating hydrocarbons supported on an inorganic oxide carrier, which comprises (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) selected from the group consisting of mercapto-carboxylic acids 20 represented by the general formula, $\text{HS}-(\text{CH}_2)_n-\text{COOR}$ (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonaceous radical of 1 to 10 carbon atoms); bivalent mercaptans represented by the general formula, $\text{HS}-\text{R}'-\text{SH}$ (wherein R' is a bivalent hydrocarbonaceous radical); aminosubstituted mercaptans represented by the general formula, $\text{H}_2\text{N}-\text{R}'-\text{SH}$ (wherein R' is as defined above); and 25 thiocarboxylic acids represented by the general formula, $\text{R}''-\text{COSH}$ (wherein R'' is a monovalent hydrocarbonaceous radical). The second aspect of this invention relates to a method of activating the catalyst as defined above which comprises treating it in the presence of hydrogen gas at a temperature in the range from room temperature to 400°C.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

As is well known, alumina, silica-alumina, titania and others are used as the inorganic oxide carrier for 35 catalysts of this type. Of these, alumina and silica-alumina are the most typical examples.

It is also known that molybdenum and/or tungsten are preferable as the active metal of Group VI, and cobalt and/or nickel are preferred examples of the active metal of Group VIII. The oxides of these metals may be used either alone or in combination.

The catalyst of this invention may also contain, as active component, oxide of phosphorus in addition to 40 oxides of Group VI and Group VIII metals. Phosphorus may be deposited on the carrier either separately or simultaneously with the active metals. In the latter case in which a solution containing all the active components is used for impregnation, the largest possible amount of phosphorus that can be included in the catalyst is 8 weight % as P_2O_5 because the treating solution becomes more viscous as its phosphorus content increases, making impregnation increasingly less effective.

45 As preferable examples of the sulfurizing agents, there may be mentioned the following compounds: mercapto-carboxylic acids represented by the general formula, $\text{HS}-(\text{CH}_2)_n\text{COOR}$ (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonyl group of 1 to 10 carbon atoms), such as mercaptoacetic acid (HSCH_2COOH), β -mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{COOH}$), alkali metal, alkaline earth metal salts 50 thereof, methyl mercaptoacetate ($\text{HSCH}_2\text{COOCH}_3$), ethyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), ethylhexyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_6\text{H}_{13}$) and methyl 3-mercaptopropionate $\text{HSCH}_2\text{CH}_2\text{COOCH}_3$; bivalent mercaptans represented by the general formula, $\text{HS}-\text{R}'-\text{SH}$ (wherein R' is a bivalent hydrocarbonaceous radical), such as ethanedithiol ($\text{HSCH}_2\text{CH}_2\text{SH}$) and 1,4-butanedithiol ($\text{HS}(\text{CH}_2)_4\text{SH}$); amino-substituted mercaptans represented by the general formula, $\text{H}_2\text{N}-\text{R}'-\text{SH}$ (wherein R' is as defined above), such as 2-aminoethanethiol ($\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$) and 4-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$); and thiocarboxylic acids 55 represented by the general formula, $\text{R}''-\text{COSH}$ (wherein R'' is a monovalent hydrocarbonaceous radical), such as thioacetic acid (CH_3COSH) and thiobenzoic acid ($\text{C}_6\text{H}_5\text{COSH}$).

A solution of the above-mentioned sulfurizing agent (mercapto-carboxylic acids and others) is soaked

by impregnation into an inorganic carrier bearing at least one member selected from the metals in the Periodic Table's Groups VI and VIII. In this case, use of an aqueous solution is most advantageous in terms of cost.

The preferable amount of sulfurizing agent (mercapto-carboxylic acids and others) to be included is 1 to 3 equivalent proportions based on the weight required for converting the Group VI and/or VIII metals to a sulfurized state highly active for hydrogenation (for example, MoS_2 , WS_2 , CoS and NiS). A smaller amount results in lower catalytic activity, while use of a larger amount is uneconomical because no marked enhancement of activity cannot be expected.

Some catalysts soaked with a solution of sulfurizing agent show activity without any further treatment; in other cases, however, activity can be exhibited by removing the solvent used for dissolving the sulfurizing agent, followed by treatment in the presence of hydrogen gas at a temperature in the range from room temperature to 400°C (the solvent removal may be performed during the activation step in the presence of hydrogen gas).

During the activation step in the presence of hydrogen gas, the sulfurizing agent attached to the active metal through coordinate bond undergoes hydrogenolysis, converting the metal component into sulfided form which is an active species for hydrogenation. In effecting this activation process, there is no specific limitation upon the reaction pressure, and presence of hydrocarbons in the reaction system causes no problem. Hence, this step may be carried out in the reactor used for hydrocarbon hydrotreatment or in a separate activation apparatus.

Activation is conducted at a temperature in the range from room temperature to 400°C , preferably in the range from 100 to 300°C . A treating temperature higher than 400°C results in lowered catalytic activity.

The catalysts prepared by the method of this invention show higher activity in hydrodesulfurization of hydrocarbon oil than those sulfurized by the conventional method. The reason is not absolutely clear yet, but it may be assumed that the sulfurizing agent used herein (mercapto-carboxylic acids and others) is attached to the Group VI and/or VIII metal through coordinate bond and this is effective in forming the metal sulfides favorable in the succeeding activation step.

The following Examples and Comparative Examples will further illustrate the invention.

Example 1

Twenty grams of a commercial catalyst containing 15 weight % of MoO_3 and 4 weight % of CoO supported on γ -alumina (KF-742; product of Nippon Ketjen Co., Ltd.) was thoroughly impregnated with 12 ml of an aqueous solution containing 6.0 g mercaptoacetic acid (d^{20}_4 : 1.33) and dried at 80°C for 16 hours, giving catalyst A_1 . Catalysts A_2 and A_3 were prepared in much the same manner as above, except that 9.0 g and 12.0 g of mercaptoacetic acid were used, respectively. Catalyst A_4 was prepared by impregnating 20 g of the commercial catalyst (KF-742) with 12 ml of an aqueous solution containing 7.5 g mercaptoacetic acid, drying at 80°C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of mercaptoacetic acid loaded on catalysts A_1 , A_2 , A_3 and A_4 were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS_2 and CoS .

Separately, 500 g of an alumina carrier (specific surface area: $310\text{ m}^2/\text{g}$; pore volume: 0.70 ml/g) used in KF-742 was impregnated with a solution prepared from 111 g ammonium paramolybdate, 101 g nickel nitrate hexahydrate 150 g conc. ammonia-water and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 15 weight % of MoO_3 and 4 weight % of NiO . This base catalyst was then treated in the same manner as above to include varying amounts of mercaptoacetic acid, affording catalysts A_5 , A_6 , A_7 and A_8 .

The amounts of mercaptoacetic acid loaded on catalysts A_5 , A_6 , A_7 and A_8 were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS_2 and NiS .

In addition, 20 g of the commercial catalyst (KF-742) was thoroughly impregnated with 12 ml of an aqueous solution containing 10.0 g mercaptopropionic acid (d^{20}_4 : 1.22) and dried at 80°C for 16 hours, giving catalyst A_9 .

The amount of mercaptopropionic acid included in this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS_2 and CoS .

(Activation)

Three milliliters each of the catalysts prepared above (A₁, A₂, A₃, A₄, A₅, A₆, A₇ and A₈) was charged
 5 in a fixed-bed flow reactor made of stainless steel and activated under the conditions shown below.

Amounts of catalyst 3 ml
 Pressure Atmospheric pressure
 Hydrogen flow rate 4.8 NI/hr
 Reaction time 3 hours
 10 Reaction temperature 200 °C

(Activity evaluation)

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The catalysts thus activated were used for hydrodesulfurization of straight-run gas oil distilled from Kuwait crude oil: hereinafter abbreviated as KSRGO. For catalyst A₂, the substance not subjected to the activation process (referred to as catalyst A₂) was also tested in the same way as above. The properties of the KSRGO used for the reaction were:

20 Specific gravity (15/4 °C) 0.848
 Sulfur (% by weight) 1.61
 Nitrogen (ppm by weight) 157
 Initial boiling point (° C) 211
 50 vol-% boiling point (°C) 340
 25 Final boiling point (° C) 406

The reaction was conducted under the conditions shown below using a fixed-bed reactor.

Amount of catalyst 3 ml
 Liquid space velocity of feed oil 2.0 hr⁻¹
 Pressure (hydrogen pressure) 30 kg/cm²
 30 Reaction temperature 330°C
 Hydrogen/oil ratio 300 NI/l
 Reaction time 8 hours

Hydrotreated oil samples were taken from reactor at an interval of two hours for determination of sulfur content. The average desulfurization rate obtained from the oil analysis for 4 hours, 6 hours and 8 hours
 35 after the start of reaction is shown in Table 1.

Comparative Example 1

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The catalysts of MoO₃/CoO and MoO₃/NiO types (hereinafter abbreviated as Mo/Co and Mo/Ni types) used in Example 1 and 2 were subjected to (presulfiding) sulfurization using n-butylmercaptan diluted with KSRGO, and tested for hydrodesulfurization activity.

45

(Sulfurizing treatment)

Sulfurizing agent 3 wt-% n-butylmercaptan in KSRGO
 Amount of catalyst 3 ml
 50 Liquid space velocity of feed oil 2.0 hr⁻¹
 Reaction pressure 30 Kg/cm²
 Reaction temperature 316°C
 Hydrogen/oil ratio 300 NI/l
 Reaction time 8 hours

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(Activity evaluation)

Catalytic activity was evaluated under the same conditions as in Example 1. The average desulfurization rate for 4 hours, samples taken 4 hours, 6 hours and 8 hours after the start of reaction is shown in Table 1.

For both of the Mo/Co and Mo/Ni types, catalysts containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than those sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO Light. With the catalysts of Mo/Co type, addition of mercaptoacetic acid in an amount of 1.2 times the theoretical weight required to convert the two metals into MoS_2 and CoS suffices, with no marked enhancement of activity being observed with a larger amount. Catalyst A'_2 was slightly lower in activity than catalyst A_2 , but showed higher activity than catalysts sulfurized with n-butylmercaptan by the conventional method. With the catalysts of Mo/Ni type, on the other hand, the optimum amount of mercaptoacetic acid to be added was somewhat larger than with catalysts of Mo/Co type, but did not exceed a level of 1.8 times the theoretical weight.

Results of Activity Evaluation Using KSRGO

Table 1-(1)

(Mo/Co type)

| Catalyst | A_1 | A_2 | A'_2 | A_3 | A_4 | Sulfurized with n-BM(*) |
|------------------------------------|-------|-------|--------|-------|-------|-------------------------|
| Content of mercaptoacetic acid(**) | x1.2 | x1.8 | x1.8 | x2.4 | x3.0 | — |
| Rate of desulfurization (%) | 88.2 | 87.5 | 86.7 | 87.3 | 87.3 | 82.7 |

Table 1-(2)

(Mo/Ni type)

| Catalyst | A_5 | A_6 | A_7 | A_8 | Sulfurized with n-BM(*) |
|------------------------------------|-------|-------|-------|-------|-------------------------|
| Content of mercaptoacetic acid(**) | x1.2 | x1.8 | x2.4 | x3.0 | — |
| Rate of desulfurization (%) | 81.2 | 84.2 | 83.9 | 83.7 | 79.1 |

Table 1-(3)

(Mo/Co type)

| Catalyst | A_9 | Sulfurized with n-BM(*) |
|--|-------|-------------------------|
| Content of mercaptopropionic acid (**) | x1.3 | — |
| Rate of desulfurization (%) | 87.5 | 82.7 |

(*) Sulfurized with 3 (wt)% n-butylmercaptan in KSRGO.

(**) Factor based on the theoretical weight required for conversion into MoS_2 , CoS and NiS .

[The same applies to the subsequent tables for (*) and (**).]

Example 2

One hundred grams of γ -alumina carrier (specific surface area: 280 m²/g; pore volume: 0.75 ml/g) was impregnated with 80 ml of an aqueous solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % of MoO₃, 4 weight % of NiO and 7 weight % of P₂O₅. This base catalyst (20 g) was thoroughly impregnated with 10 ml of an aqueous solution containing 7.3 g mercaptoacetic acid and dried at 100°C for 16 hours, affording catalyst B₁.

Catalysts B₂ and B₃ were prepared in much the same maner as above, except that 11.0 g and 14.6 g of 100% mercaptoacetic acid were used, respectively, in place of the aqueous solution.

The amounts of mercaptoacetic acid loaded on catalysts B₁, B₂ and B₃ were respectively 1.0, 1.5 and 2.0 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Separately, 20 g of the calcined catalyst prepared above was thoroughly impregnated with an aqueous solution containing 11.7 g mercaptopropionic acid and dried at 100°C for 16 hours, giving catalyst B₄. The amount of mercaptopropionic acid loaded on this catalyst was 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

(Activity evaluation)

Catalysts B₁, B₂, B₃ and B₄ were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 1. The average desulfurization rates are shown in Table 2.

Comparative Example 2

The base catalyst of MoO₃/NiO/P₂O₅ type (hereinafter abbreviated as Mo/Ni/P type) used in Example 2 was sulfurized in the same manner as in Comparative Example 2, and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average desulfurization rate is also shown in Table 2.

Table 2 Results of Activity Evaluation Using KSRGO

| Catalyst | B ₁ | B ₂ | B ₃ | B ₄ | Sulfurized with n-BM(*) |
|----------------------------------|------------------------|----------------|----------------|--|-------------------------|
| Content of sulfurizing agent(**) | HSCH ₂ COOH | | | HSCH ₂ CH ₂ COOH | — |
| | x1.0 | x1.5 | x2.0 | x1.5 | |
| Rate of desulfurization (%) | 89.6 | 93.5 | 93.0 | 93.4 | 73.5 |

The catalysts containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO. Data of the catalysts containing mercaptoacetic acid indicate that addition of the acid in an amount of 1.5 times the theoretical weight required to convert the two metals into MoS₂, NiS and CoS suffices, with no marked enhancement of activity being observed with larger amounts. Excessively large amounts of sulfurizing agent included in a catalyst not only results in its waste, but also requires two or more steps for impregnation.

Example 3

Twenty grams of commercial catalyst (the same type as used in Example 1) was thoroughly impregnated with 10.4 g of 100% methyl mercaptoacetate and dried at 80°C for 16 hours, giving catalyst

C₁. Catalyst C₂ was prepared in much the same manner as above, except that 11.7 g of ethyl mercaptoacetate was used as sulfurizing agent. Catalyst C₃ was prepared by impregnating 20 g of the above commercial catalyst with 20.0 g of 2-ethylhexyl mercaptoacetate, drying at 80°C for 16 hours, and repeating the impregnation and drying steps once again.

5 The amounts of mercaptoacetate loaded on catalysts C₁, C₂ and C₃ were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

Separately, the same commercial catalysts as above was thoroughly impregnated with 11.7 g of methyl 3-mercapto propionate and dried at 80°C for 16 hours, giving catalyst C₄. The amount of methyl 3-mercaptopropionate loaded on this catalyst was 1.8 times the theoretical amount required to convert the two
10 metals into MoS₂ and CoS.

In addition, 500 g of alumina carrier (the same type as used in Example 1 for the preparation of catalysts A₅ through A₈) was impregnated with a solution prepared from 111 g ammonium paramolybdate, 101 g nickel nitrate hexahydrate and 150 g conc. ammonia water, dried at 110°C for 16 hours and calcined at 500 C for two hours, giving a catalyst containing 15 weight % of MoO₃ and 4 weight % of NiO. This base
15 catalyst was then activated in the same manner as in Example 1 to include 10.4 g methyl mercaptoacetate, 11.7 g ethyl mercaptoacetate or 20.0 g 2-ethylhexyl mercaptoacetate, affording catalysts C₅, C₆ and C₇, respectively.

The amounts of mercaptoacetate loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

20 Furthermore, 20 g of the above base catalyst was thoroughly impregnated with 11.7 g methyl 3-mercaptopropionate and dried at 80°C for 16 hours, giving catalyst C₈.

The amount of methyl 3-mercaptopropionate loaded on this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts C₁, C₂, C₃, C₄, C₅, C₆, C₇ and C₈ prepared above were activated in the same manner as in
25 Example 1 and used for hydrodesulfurization of KSRGO under the same conditions. The average desulfurization rates are shown in Table 3.

30 Comparative Example 3

The catalysts of Mo/Co and Mo/Ni types used in Example 3 were sulfurized in the same manner as in Comparative Example 1, and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average desulfurization rates are also shown in Table 3.

35 For both of the Mo/Co and Mo/Ni types, catalysts containing a mercaptoacetate or mercaptopropionate showed nearly the same activity as those sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

40 Example 4

One hundred grams of γ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%
45), 16.5 g 85% of phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % MoO₃, 4 weight % NiO and 7 weight % P₂O₅. This base catalyst (30 g) was then impregnated with

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(Mo/Co type)

Table 3-(1)

| Catalyst | C ₁ | C ₂ | C ₃ | C ₄ | Sulfurized with n-BM(*) |
|----------------------------------|-----------------------------|----------------------------|---------------------------------|-------------------------------|----------------------------|
| Mercurio- carboxylate | Methyl mer- captoacetate | Ethyl mer- captoacetate | 2-Ethylhexyl mercaptoacetate | Methyl 3-mer- captoacetate | — |
| Amount (**) | x1.8 | x1.8 | x1.8 | x1.8 | — |
| Rate of desul- furization (%) | 82.2 | 82.7 | 83.3 | 83.7 | 82.7 |

(Mo/Ni type)

Table 3-(2)

| Catalyst | C ₅ | C ₆ | C ₇ | C ₈ | Sulfurized with n-BN(*) |
|----------------------------------|-----------------------------|----------------------------|---------------------------------|----------------------------------|----------------------------|
| Mercapto- carboxylate | Methyl mer- captoacetate | Ethyl mer- captoacetate | 2-Ethylhexyl mercaptoacetate | Methyl 3-mer- captopropionate | — |
| Amount (**) | x1.8 | x1.8 | x1.8 | x1.8 | |
| Rate of desul- furization (%) | 78.9 | 80.8 | 79.7 | 79.3 | 79.1 |

Table 4
(Mo/Ni/P type)

| Catalyst | D ₁ | D ₂ | D ₃ | D ₄ | Sulfurized with n-EM(*) |
|----------------------------------|-----------------------------|----------------------------|---------------------------------|-------------------------------|----------------------------|
| Mercapto- carboxylate | Methyl mer- captoacetate | Ethyl mer- captoacetate | 2-Ethylhexyl mercaptoacetate | Methyl 3-mer- captoacetate | — |
| Amount (**) | x1.5 | x1.5 | x1.5 | x1.5 | |
| Rate of desul- furization (%) | 80.3 | 78.9 | 80.8 | 76.7 | 73.5 |

15.8 g methyl mercaptoacetate and dried at 100°C for 16 hours, affording catalyst D₁. Catalyst D₂ was prepared in much the same manner as above, except that 17.9 g of ethyl mercaptoacetate was used in place of methyl mercaptoacetate. Catalyst D₃ was prepared by impregnating the base catalyst (30 g) with 35.8 g 2-ethylhexyl mercaptoacetate, drying at 100°C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of mercaptoacetate loaded on catalysts D₁, D₂ and D₃ were 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

In addition, catalyst D₄ was prepared by impregnating the above base catalyst (30 g) with 21.0 g methyl 3-mercaptopropionate and drying at 100°C for 16 hours. The amount of methyl 3-mercaptopropionate loaded on this catalyst was 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts D₁, D₂, D₃ and D₄ prepared above were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 2. The average rates of desulfurization are shown in Table 4.

Comparative Example 4

The base catalyst of Mo/Ni/P type used in Example 4 was sulfurized in the same manner as in Comparative Example 2 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average rate of desulfurization is also shown in Table 4.

The catalysts of Mo/Ni/P type containing a mercaptoacetate or mercaptopropionate showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

Example 5

Thirty grams of commercial catalyst containing 17 wt% of MoO₃ and 4 wt% of CoO supported on γ -alumina (KF-707: product of Nippon Ketjen Co. Ltd.) was impregnated with 15 ml of ethanolic solution containing 7.9 g ethanedithiol or 10.2 g 1,4-butanedithiol, and dried at 80 C for 16 hours, giving catalysts E₁ and E₂, respectively.

The amounts of dithiol loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

Catalysts E₁ and E₂ prepared above were activated in the same manner as in Example 1 and used for hydrodesulfurization of KSRGO under the same conditions. The average rates of desulfurization are shown in Table 5.

Comparative Example 5

The base catalyst of Mo/Co type used in Example 5 was sulfurized in the same manner as in Comparative Example 2 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 5.

Table 5

| Catalyst | E ₁ | E ₂ | Sulfurized with n-BM(*) |
|-----------------------------|----------------|--------------------|-------------------------|
| Bivalent mercaptan | Ethane-dithiol | 1,4-Butane-dithiol | — |
| Amount(**) | x1.3 | x1.3 | |
| Rate of desulfurization (‡) | 90.1 | 86.9 | 81.5 |

The catalysts of Mo/Co type containing ethanedithiol or 1,4-butanedithiol showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

5 Example 6

One hundred grams of γ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % MoO_3 , 4 weight % NiO and 7 weight % P_2O_5 . This base catalyst (30 g) was then impregnated with 12 ml of ethanolic solution containing 7.0 g ethanedithiol or 9.1 g 1,4-butanedithiol, and dried at 100°C for 16 hours, affording catalysts F_1 and F_2 , respectively.

The amounts of dithiol loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into MoS_2 and NiS.

Catalysts F_1 and F_2 prepared above were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulfurization are shown in Table 6.

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Comparative Example 6

The base catalyst of Mo/Ni/P type used in Example 6 was sulfurized in the same manner as in Comparative Example 2 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 6.

Table 6

| Catalyst | F_1 | F_2 | Sulfurized with n-BM(*) |
|-----------------------------|----------------|--------------------|-------------------------|
| Bivalent mercaptan | Ethane-dithiol | 1,4-Butane-dithiol | — |
| Amount(**) | x1.5 | x1.5 | |
| Rate of desulfurization (%) | 94.1 | 90.9 | 73.5 |

The catalysts of Mo/Ni/P type containing ethanedithiol or 1,4-butanedithiol showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

Example 7

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Thirty grams of commercial catalyst (the same type as used in Example 5) was impregnated with 13.0g 2-aminoethanethiol or 20.8 g 4-aminothiophenol, and dried at 80°C for 16 hours, giving catalysts G_1 and G_2 , respectively.

The amounts of amino-substituted mercaptan included in these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS_2 and CoS.

Catalysts G_1 and G_2 prepared above were activated in the same manner as in Example 1 and used for hydrodesulfurization of KSRGO under the same conditions. The average rates of desulfurization are shown in Table 7.

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Comparative Example 7

The base catalyst of Mo/Co type used in Example 7 was sulfurized in the same manner as in Comparative Example 1 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 7.

The catalysts of Mo/Co type containing 2-aminoethanethiol or 4-aminothiophenol showed higher activity than that sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

Table 7

| Catalyst | G ₁ | G ₂ | Sulfurized with n-BM(*) |
|-----------------------------|--------------------|-------------------|-------------------------|
| Amino-substituted mercaptan | 2-Aminoethanethiol | 4-Aminothiophenol | — |
| Amount(**) | x1.8 | x1.8 | |
| Rate of desulfurization (%) | 81.7 | 85.0 | 81.5 |

Example 8

One hundred grams of γ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a base catalyst containing 20 weight % MoO₃, 4 weight % NiO and 7 weight % P₂O₅. Catalysts H₁ and H₂ were prepared by impregnating the base catalyst (30 g) obtained above with 30 ml of aqueous solution containing 11.5 g 2-aminoethanethiol or 18.6 g 4-aminothiophenol, drying at 100°C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of amino-substituted mercaptan loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts H₁ and H₂ prepared above were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulfurization are shown in Table 8.

Comparative Example 8

The base catalyst of Mo/Ni/P type used in Example 8 was sulfurized in the same manner as in Comparative Example 1 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 8.

Table 8

| Catalyst | H ₁ | H ₂ | Sulfurized with n-BM(*) |
|-----------------------------|--------------------|-------------------|-------------------------|
| Amino-substituted mercaptan | 2-Aminoethanethiol | 4-Aminothiophenol | — |
| Amount(**) | x1.5 | x1.5 | |
| Rate of desulfurization (%) | 83.1 | 90.6 | 73.5 |

The catalysts of Mo/Ni/P type containing 2-aminoethanethiol or 4-aminothiophenol showed higher activity than the catalyst that sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

5 Example 9

Thirty grams of commercial catalyst (the same type as used in Example 5) was impregnated with 15 ml of ethanolic solution containing 12.7 g thioacetic acid or 23.0 g thiobenzoic acid; and dried at 80°C for 10 16 hours, giving catalysts I₁ and I₂, respectively.

The amounts of thio-acid loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

Catalysts I₁ and I₂ prepared above were activated in the same manner as in Example 1 and used for hydrodesulfurization of KSRGO under the same conditions. The average rates of desulfurization are shown 15 in Table 9.

Comparative Example 9

20 The base catalyst of Mo/Co type used in Example 7 was sulfurized in the same manner as in Comparative Example 1 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 9.

The catalysts of Mo/Co type containing thioacetic acid or thiobenzoic acid showed higher activity than 25 that sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

Table 9

| Catalyst | I ₁ | I ₂ | Sulfurized with n-BM(*) |
|--------------------------------|-----------------|------------------|-------------------------|
| Thio-acid | Thioacetic acid | Thiobenzoic acid | — |
| Amount(**) | x1.8 | x1.8 | |
| 35 Rate of desulfurization (%) | 85.1 | 82.0 | 31.5 |

40 Example 10

One hundred grams of γ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % MoO₃, 4 weight % NiO and 7 weight % P₂O₅. This base catalyst (30 g) was impregnated with 15 ml of ethanolic solution containing 11.3 g thioacetic acid or 20.6 g thiobenzoic acid, and dried at 110°C for 16 hours, giving catalysts J₁ and J₂, respectively.

The amounts of thio-acid loaded on these catalysts were 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts J₁ and J₂ prepared above were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 1. The average rates of desulfurization are shown in Table 10.

Comparative Example 10

The base catalyst of Mo/Ni/P type used in Example 10 was sulfurized in the same manner as in Comparative Example 1 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The rate of desulfurization is also shown in Table 10.

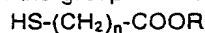
Table 10

| Catalyst | J ₁ | J ₂ | Sulfurized with n-BM(*) |
|-----------------------------|-----------------|------------------|-------------------------|
| Thio-acid | Thioacetic acid | Thiobenzoic acid | — |
| Amount(**) | x1.5 | x1.5 | |
| Rate of desulfurization (%) | 74.8 | 90.5 | 73.5 |

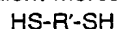
The catalysts of Mo/Ni/P type containing thioacetic acid or thiobenzoic acid showed higher activity than that sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

Claims

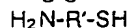
1. Catalyst for hydrotreating hydrocarbons supported on an inorganic oxide carrier, which comprises (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) selected from the group consisting of mercapto-carboxylic acids represented by the following general formula:



(wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonaceous radical of 1 to 10 carbon atoms); bivalent mercaptans represented by the following general formula:



(wherein R' is a bivalent hydrocarbonaceous radical); aminosubstituted mercaptans represented by the following general formula:



(wherein R' is as defined above); and thiocarboxylic acids represented by the following general formula:



(wherein R'' is a monovalent hydrocarbonaceous radical).

2. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said inorganic oxide carrier is made of at least one material selected from the group consisting of alumina, silica-alumina and titania.

3. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said Group VI metal is at least one member selected from the group consisting of molybdenum and tungsten and said Group VIII metal is at least one member selected from the group consisting of cobalt and nickel.

4. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said Group VI metal is at least one member selected from the group consisting of molybdenum and tungsten, said Group VIII metal is at least one member selected from the group consisting of cobalt and nickel and said catalyst also contains phosphorus as a component element.

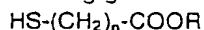
5. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said mercapto-carboxylic acid represented by the general formula, $\text{HS}-(\text{CH}_2)_n-\text{COOR}$ (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonaceous radical of 1 to 10 carbon atoms), is at least one member selected from the group consisting of mercaptoacetic acid (HSCH_2COOH), β -mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{COOH}$), alkali metal, alkaline earth metal and ammonium salts thereof, methyl mercaptoacetate ($\text{HSCH}_2\text{COOCH}_3$), ethyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), ethylhexyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_8\text{H}_{17}$) and methyl 3-mercaptopropionate ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$).

6. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said bivalent mercaptan represented by the general formula, HS-R'-SH (wherein R' is a bivalent hydrocarbonaceous radical), is at least one member selected from the group consisting of ethanedithiol ($\text{HSCH}_2\text{CH}_2\text{SH}$) and 1,4-butanedithiol ($\text{HS}(\text{CH}_2)_4\text{SH}$).

5 7. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said amino-substituted mercaptan represented by the general formula, $\text{H}_2\text{N-R'-SH}$ (wherein R' is a bivalent hydrocarbonaceous radical), is at least one member selected from the group consisting of 2-aminoethanethiol ($\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$) and 4-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$).

8. The catalyst for hydrotreating hydrocarbons as defined in claim 1, wherein said thiocarboxylic acid represented by the general formula, R''-COSH (wherein R'' is a monovalent hydrocarbonaceous radical), is at least one member selected from the group consisting of thioacetic acid (CH_3COSH) and thiobenzoic acid ($\text{C}_6\text{H}_5\text{COSH}$).

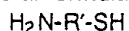
9. Method of activating hydrotreating catalysts for hydrocarbons supported on an inorganic oxide carrier by treatment at a temperature in the range from room temperature to 400°C in the presence of hydrogen gas, said catalyst comprising (a) at least one member selected from the group consisting of oxides of metals in the Periodic Table's Groups VI and VIII, and (b) at least one organic compound having a mercapto radical or radicals ($-\text{SH}$) selected from the group consisting of mercapto-carboxylic acids represented by the following general formula:



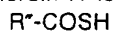
20 (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonaceous radical of 1 to 10 carbon atoms); bivalent mercaptans represented by the following general formula:



(wherein R' is a bivalent hydrocarbonaceous radical substituted mercaptans represented by the following general formula:



(wherein R' is as defined above); and thiocarboxylic acids represented by the following general formula:



(wherein R'' is a monovalent hydrocarbonaceous radical

30 10. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said inorganic oxide carrier is made of a material selected from the group consisting of alumina, silica, alumina and titania.

11. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said Group VI metal is at least one member selected from the group consisting of molybdenum and tungsten and said Group VIII metal is at least one member selected from the group consisting of cobalt and nickel.

12. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said Group VI metal is at least one member selected from the group consisting of molybdenum and tungsten, said Group VIII metal is at least one member selected from the group consisting of cobalt and nickel, and said catalyst also contains phosphorus as a component element.

13. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said mercaptocarboxylic acid represented by the general formula, $\text{HS}(\text{CH}_2)_n-\text{COOR}$ (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or naphthene hydrocarbonaceous radical of 1 to 10 carbon atoms), is at least one member selected from the group consisting of mercaptoacetic acid (HSCH_2COOH), β -mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{COOH}$), alkali metal, alkaline earth metal ($\text{HSCH}_2\text{COOCH}_3$), ethyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), ethylhexyl mercaptoacetate ($\text{HSCH}_2\text{COOC}_3\text{H}_7$) and methyl 3-mercaptopropionate ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$).

14. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said bivalent mercaptan represented by the general formula, HS-R'-SH (wherein R' is a bivalent hydrocarbonaceous radical), is at least one member selected from the group consisting of ethanedithiol ($\text{HSCH}_2\text{CH}_2\text{SH}$) and 1,4-butanedithiol ($\text{HS}(\text{CH}_2)_4\text{SH}$).

15. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said amino-substituted mercaptan represented by the general formula, $\text{H}_2\text{N-R'-SH}$ (wherein R' is a bivalent hydrocarbonaceous radical), is at least one member selected from the group consisting of 2-aminoethanethiol ($\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$) and 4-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$).

16. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said thiocarboxylic acid represented by the general formula, $R^{\cdot}-COSH$ (wherein R^{\cdot} is a monovalent hydrocarbonaceous radical), is at least one member selected from the group consisting of thioacetic acid (CH_3COSH) and thiobenzoic acid (C_6H_5COSH).

5 17. The method of activating hydrotreating catalysts for hydrocarbons as defined in claim 9, wherein said treating temperature is in the range from 100 to 300°C.

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 88303592.5

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| X | GB - A - 1 575 434 (GULF RE-SEARCH & DEVELOPMENT COMPANY) * Page 1, line 56 - page 2, line 24; claims * | 1-3,5-7,9-11,13-17 | B 01 J 31/02 B 01 J 37/20 B 01 J 27/049 B 01 J 27/051 |
| -- | | | |
| A | DE - A - 2 316 029 (UNIVERSAL OIL PRODUCTS) * Page 14, lines 1-26; claims * | 1-3,9-11,17 | C 10 G 45/08 C 10 G 49/04 |
| -- | | | |
| A | EP - A1 - O 181 254 (EURECAT EUROPEENNE DE RETRAITEMENT DE CATALYSEURS) * Claims * | 1-3,9-11,17 | |
| -- | | | |
| A | US - A - 3 850 846 (KRAVITZ et al.) * Column 1, lines 65-72; column 2, lines 35-57; claims * | 1-3,9-11,17 | TECHNICAL FIELDS SEARCHED (Int. Cl. 4) B 01 J C 10 G |
| ---- | | | |
| The present search report has been drawn up for all claims | | | |
| Place of search VIENNA | | Date of completion of the search 14-07-1988 | Examiner TENGLER |
| CATEGORY OF CITED DOCUMENTS | | | |
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